present technique appears to be better suited for interpreting unambiguously the subsequent step in complex formation.

The reaction of NPA with the basic form of the α-amino group of a peptide provides both a measure of the reactivity of the group and a means of modifying it by acetylation. The reaction should be able to supply valuable information about molecules containing reactive groups belonging to both the categories represented by the α-amino group and the imidazole group. With excess NPA the former class should be converted to the subsequently unreactive acetylated form. If such a flexible use of the NPA technique were not suitable for a particular investigation, presumably a purely catalytic technique could be used. Speck and Forist[19] have shown that cupric ion inhibits the glycinate-catalyzed dealdolization of diacetone alcohol.

Although CuGG does not react with NPA at a measurable rate, conversion to basic complexes of the type of CuGGOH⁻ leads to rapid splitting of the NPA. In a subsequent paper this finding will be described in detail, together with other observations on complexes of peptides with Cu(II) ion.

Acknowledgments.—We wish to thank Dr. Melvin Fried for the gift of acetylglycylglycine and for helpful discussions. The technical assistance of Miss Reta Roth and Miss Shirley Light is gratefully acknowledged.

[19] J. C. Speck, Jr., and A. A. Forist, THIS JOURNAL, **79**, 4659 (1957).

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The Stability of Platinum–Styrene Complexes

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The reaction of styrene with ethylene platinous chloride was used to prepare a series of substituted styrene–platinum complexes of the general formula $(X{-}C_6H_4CH{=}CH_2PtCl_2)_2$, where X = H, 3-Cl, 3-$CH_3O$, 4-$CH_3O$, 3-$NO_2$, 4-$NO_2$ and 4-CH_3. The analogous 1-dodecene complex also was prepared. When dissolved in alcoholic hydrogen chloride the dimeric complex splits into an ionic one, *e.g.*, $(C_{12}H_{24}PtCl_2)_2 + 2HCl \rightarrow 2H(C_{12}H_{24}PtCl_3)$. The addition of styrene to this system results in the equilibrium: $X{-}C_6H_4CH{=}CH_2 + (C_{12}H_{24}PtCl_3)^- \rightleftarrows (X{-}C_6H_4CH{=}CH_2PtCl_3)^- + C_{12}H_{24}$. The equilibrium constant for this reaction (starting from either side) was evaluated by means of ultraviolet spectrophotometry. When this constant was plotted against the Hammett sigma values for the various substituents a U-shaped curve resulted. All substituents were stabilizing relative to styrene. This fact is consistent with the presence of a double bond between the platinum and the olefinic ligand, the sigma and pi bonds being affected approximately equally but in opposite directions by the substituent.

Introduction and Background

The Structure of Platinum–Olefin Complexes.—A study of platinum–olefin coördination complexes was undertaken in an effort to obtain quantitative data on the factors affecting the stability of the metal–olefin bond. The complexes under consideration are of two types, ionic complexes, such as Zeise's salt,[1] $K(C_2H_4PtCl_3)$, and non-ionic, dimeric complexes, such as ethylene platinous chloride,[2] $(C_2H_4PtCl_2)_2$.

The concept of the bonding between the metal and the olefin as developed by Dewar[3] to describe the silver–olefin complexes was extended by Chatt and Duncanson[4] to the platinum compounds. The platinum ion is divalent; its complexes are square planar and involve $5d6s6p^2$ hybrid orbitals of platinum. In both the ionic and non-ionic complexes the olefin is oriented perpendicularly to the plane of the complex. The bonding pi-electrons of the olefin overlap an unoccupied $5d6s6p^2$ hybrid orbital of platinum, forming a sigma-bond. The platinum in turn donates a pair of electrons in a 5d6p hybrid orbital into the empty anti-bonding pi-orbital of the olefin, forming a pi-bond. The double bond which results frequently has been called a dative double bond.

Baenziger, Dempsey and Holden[5,6] showed, by means of X-ray studies on the analogous palladium complexes, that the dimeric compounds have a bridged structure with two chloride ions linking the two central atoms. This is represented by the structure I, where Un represents any coördinating olefin.[7]

Evaluation of Relative Stabilities.—One of the most striking reactions of the platinum–ethylene complexes is the rapid displacement of ethylene by another less volatile olefin and the formation of a new complex

$$\mathrm{Un} + (C_2H_4PtCl_3)^- \longrightarrow (\mathrm{UnPtCl_3})^- + C_2H \quad (1)$$

$$2\mathrm{Un} + (C_2H_4PtCl_2)_2 \longrightarrow (\mathrm{UnPtCl_2})_2 + 2C_2H_4 \quad (2)$$

Anderson[2] used these reactions to prepare complexes of various olefins including that with styrene.

It appeared reasonable that were a non-volatile olefin reacting with the complex of another high-

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[1] Zeise, *Pogg. Ann.*, **9**, 632 (1827).

[2] J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

[3] M. J. S. Dewar, *Bull. Soc. Chim.*, **18**, 71 (1951).

[4] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[5] N. C. Baenziger and J. N. Dempsey, THIS JOURNAL, **77**, 4984 (1955).

[6] N. C. Baenziger and J. R. Holden, *ibid.*, **77**, 4987 (1955).

[7] The systematic name for this structure, when Un is ethylene, is 1,3-bis-(ethylene)-2,4-dichloro-μ-dichlorodiplatinum. The systematic name for the ionic form, $K(C_2H_4PtCl_3)$, is potassium ethylenetrichloroplatinate(II).

I

boiling olefin rather than with the ethylene complex, the reaction would proceed to equilibrium, the position of which would be a measure of the relative stabilities of the two metal–olefin complexes. Accordingly, in the present work, the complex with 1-dodecene was prepared and equilibrated with a series of 3- and 4-substituted styrenes.

When 1,3-bis-(1-dodecene)-2,4-dichloro-μ-dichlorodiplatinum is dissolved in hydrochloric acid, the dimer is split to form two molecules of (1-dodecene)-trichloroplatinic(II) acid

$$(C_{12}H_{24}PtCl_2)_2 + 2HCl \longrightarrow 2H^+ + 2(C_{12}H_{24}PtCl_3)^- \quad (3)$$

This reaction is complete in excess acid. The addition of styrene leads to the equilibrium

$$X\text{–}C_6H_4\text{–}C_2H_3 + (C_{12}H_{24}PtCl_3)^- \rightleftharpoons (X\text{–}C_6H_4\text{–}C_2H_3PtCl_3)^- + C_{12}H_{24} \quad (4)$$

The expression for the equilibrium constant is

$$K = \frac{[C_{12}H_{24}][X\text{–}C_6H_4\text{–}C_2H_3PtCl_3)^-]}{[X\text{–}C_6H_4\text{–}C_2H_3][(C_{12}H_{24}PtCl_3)^-]} \quad (5)$$

The concentration of the two complexes may be evaluated by ultraviolet spectrophotometry, which thus permits the calculation of the equilibrium constant.

In general the system in equilibrium contains three species which absorb in the near ultraviolet, since 1-dodecene has insufficient absorptivity to require its consideration. The total absorbance at a given wave length then can be expressed by the equation

$$A = \epsilon_1 bc_1 + \epsilon_2 bc_2 + \epsilon_3 bc_3 \quad (6)$$

where A is the observed absorbance; ϵ_1, ϵ_2 and ϵ_3 are the molar absorptivities, and c_1, c_2 and c_3 the molar concentrations, of the 1-dodecene complex, the styrene complex and the styrene, respectively; and b is the cell thickness. (This quantity equals 1 cm. and will be omitted hereafter.)

From equation 4, $c_1 = c_0 - c_2$, where c_0 is the initial concentration of the 1-dodecene complex, and $c_3 = c_s - c_2$, where c_s is the initial concentration of the styrene. The expression for the total absorbance at the chosen wave length becomes

$$A = \epsilon_1(c_0 - c_2) + \epsilon_2 c_2 + \epsilon_3(c_s - c_2) \quad (7)$$

Solving for c_2 gives

$$c_2 = \frac{A - \epsilon_1 c_0 - \epsilon_3 c_s}{\epsilon_2 - \epsilon_1 - \epsilon_3} \quad (8)$$

The equilibrium constant can now be evaluated by substituting the concentration values into equation 5 to give

$$K = \frac{c_2^2}{(c_s - c_2)(c_0 - c_2)} \quad (9)$$

In evaluating the equilibrium constant when X = H, 4-OCH$_3$ or 4-CH$_3$ the absorbance of the styrene may be omitted because of its negligible absorptivity at the wave lengths at which the measurements are taken. If ϵ_3 is set equal to zero equation 8 becomes

$$c_2 = \frac{A - \epsilon_1 c_0}{\epsilon_2 - \epsilon_1} \quad (10)$$

Results and Discussion

Ultraviolet Absorption Spectra. Ionic Complexes.—The absorption spectra of the ionic styrene complexes, H(X-C$_6$H$_4$-C$_2$H$_3$PtCl$_3$), (Table I), are similar in certain respects to those for the styrenes themselves (Table III). In the short wave length region the position of the peak and the intensity of absorption are very close for the styrene and its complex. Nevertheless, a moderate bathochromic shift of 3–10 mμ and a slight hypsochromic effect are noted in the complexed styrenes. Much greater changes are noted in the long wave length region, where the complex absorbs much more intensely than the free styrene. The absorptivity in these regions is intense even for the complexes of those styrenes which do not exhibit a well-defined long wave length band. The shifts in the positions of the maxima cannot be classified conveniently. 3-Methoxystyrene exhibits a hypsochromic shift of 18 mμ when it is complexed, whereas 4-methoxystyrene appears to undergo a slight bathochromic shift.

TABLE I

ABSOPTION SPECTRA OF IONIC COMPLEXES, H(UnPtCl$_3$)

Un	Solvent	Long wave length Mμ	Log ε	Short wave length max. Mμ	Log ε
Styrene	HCl 1.1 mole/l.	273	3.96	250	4.03
4-Methylstyrene	HCl in ethanol 0.01 mole/l.	290	4.10	262	4.10
3-Methoxystyrene	HCl in ethanol 0.01 mole/l.	278	3.97	258	4.03
4-Methoxystyrene	HCl in ethanol 0.01 mole/l.	302	4.15	269	4.05
3-Nitrostyrene	HCl in ethanol 1.0 mole/l.	...	..	246	4.31
4-Nitrostyrene	HCl in ethanol 0.01 mole/l.	...	..	299	4.16
3-Chlorostyrene	HCl 1.0 mole/l.	265–280 Shoulder	4.0	253	4.06
1-Dodecene	HCl in ethanol 0.01 mole/l.	338	2.38	248	3.61
Ethylene	HCl 1.1 mole/l.	335	2.37	239	3.52

Covalent Complexes.—The spectra of the covalent complexes, (X-C$_6$H$_4$-C$_2$H$_3$PtCl$_2$)$_2$, (Table II), have not been studied as extensivley as those of the ionic complexes. Therefore there are insufficient data to establish firmly any significant trends. However, it appears that the more significant changes may lie again in the long wave length absorption bands, although the increase in intensity for the complexed styrene apparently is not nearly as great as in the ionic complexes.

TABLE II

ABSORPTION SPECTRA OF COVALENT COMPLEXES, (UnPtCl$_2$)$_2$

Un	Solvent	Long wave length max. Mμ	Log ε	Short wave length max. Mμ	Log ε
Styrene	*t*-Butyl alcohol	278	3.97	243	4.61
	Chloroform	283	4.22	..	..
3-Chlorostyrene	*t*-Butyl alcohol	270–280 Shoulder	~3.8	245	4.56
Ethylene	*t*-Butyl alcohol	293	3.19	243	3.70
	Chloroform	333	2.69	296	3.25

Equilibrium Constants.—The equilibrium contants for the reactions of styrenes, X-C$_6$H$_4$-C$_2$H$_3$, with (1-dodecene)-trichloroplatinic(II) acid, H(C$_{12}$H$_{24}$PtCl$_3$), in alcoholic hydrochloric acid are listed

TABLE III
ABSORPTION SPECTRA OF STYRENES

Un	Solvent	Long wave length max. Mμ	Log ε	Short wave length max. Mμ	Log ε
Styrene[8]	95% Ethanol	291	2.8	245	4.1
		282	2.9		
4-Methylstyrene	HCl in ethanol 0.01 mole/l.	295	2.84	252	4.23
		285	3.07		
3-Methoxystyrene	HCl in ethanol 0.01 mole/l.	296	3.37	250	4.04
4-Methoxystyrene	HCl in ethanol 0.01 mole/l.	290–294 Shoulder	~3.3	260	4.17
3-Nitrostyrene	HCl in ethanol 0.01 mole/l.	316	3.06	240	4.38
4-Nitrostyrene[9]	Methanol	...	..	300	4.14
3-Chlorostyrene[10]	Chloroform	...	..	250	4.18

in Table IV. The reverse reaction was run on two complexes as a check on the reliability of the method, the results being listed in Table V. The agreement between the equilibrium constants, regardless of the direction chosen, adds confidence in the values obtained. The applicability of the spectrophotometric method of analysis stems from the immense difference in the long wave length absorptivity for most of the styrenes as compared with their complexes. The dramatic change in the spectrum of the Pt(II) salt and of the *p*-methoxystyrene (as a typical example), when these moieties are complexed, is shown in Fig. 1. The formation of only a small concentration of a styrene complex causes an easily measured increase in the absorbance of the system. The reaction of styrene with the dodecene complex was used as the principal method of study because it leads to more accurate measurements than the reverse reaction, since the position of the equilibrium favors the dodecene complex. In this system, measurements can be made accurately while the concentration of the styrene is varied over a wide range. In the reverse reaction the concentration range of dodecene is much more limited because excess dodecene quickly reduces the concentration of the styrene complex beyond the point where it can be evaluated accurately.

The comparatively poor precision for the 4-nitrosytrene complex can be attributed to the rather high absorptivity in the longer wave lengths of 4-nitrostyrene compared with the other styrenes. In this case the styrene itself makes a large contribution to the total absorbance, thereby decreasing the accuracy of the measurements.

Two effects are immediately obvious from the values of the equilibrium constants. (1) 1-Dodecene forms a more stable complex in solution than any of the styrenes studied. The equilibrium ratio of the 1-dodecene complex to the unsubstituted styrene complex is about 6:1 when stoichiometric starting quantities are used. (2) The effect of substitution on the stability of the styrene complex series is small, all substituents studied exhibiting a stabilizing influence. In view of this modest effect the solvation energies of the members of reaction series require consideration. In order that the differences in stability in the series may be attributed to the electronic influences of the substituents, it is important that the change in solvation for the reactions of the styrenes with the 1-dodecene complex be very nearly the same for all members of the series. As a styrene molecule reacts with a dodecene complex ion the solvation changes will occur around the exocyclic double bond of the styrene. Since the substituents in all cases are in the 3- and 4-positions on the aromatic ring, they are distant from the point of reaction and should undergo very little change in solvation as the styrene displaces the dodecene from the complex ion. The solvation of the dodecene complex is a constant factor in each determination. Therefore, the solvation energy changes for the reaction should be nearly constant throughout the series, and the differences in stability of the styrene complexes can be attributed to the electronic effects of the ring substituents.

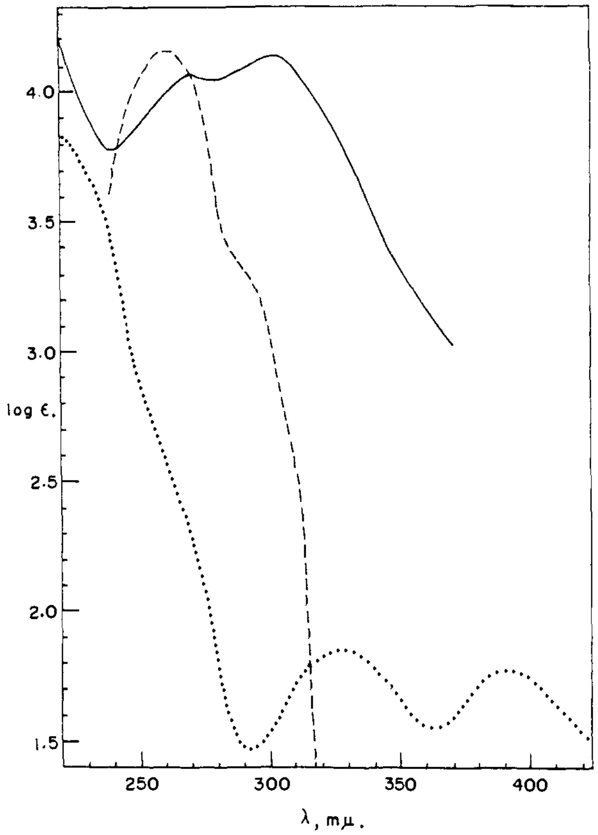

Fig. 1.—Ultraviolet spectra: . . . ., K_2PtCl_4 in H_2O; - - - -, *p*-methoxystyrene; and ———, $H(4\text{-}CH_3O\text{-}C_6H_4\text{-}C_2H_3PtCl_3)$ in 0.01 *M* ethanolic HCl.

A Hammett plot of the logarithms of the equilibrium constants *versus* the substituent sigma values forms a rather smooth curve (Fig. 2), the only point not fitting well being the one for 3-methoxystyrene. Just how strictly the curve can be interpreted is difficult to estimate because of the unusual nature of the reactions. However, it does offer a graphical presentation of the substituent effects and supports the contention that electronic effects are the determining factors with respect to the position of equilibrium.

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[8] M. T. Rogers, THIS JOURNAL, **69**, 2544 (1947).

[9] M. J. Kamlet and D. L. Glover, *ibid.*, **77**, 5696 (1955).

[10] H. A. Laitinen, F. A. Miller and T. D. Parks, *ibid.*, **69**, 2707 (1947).

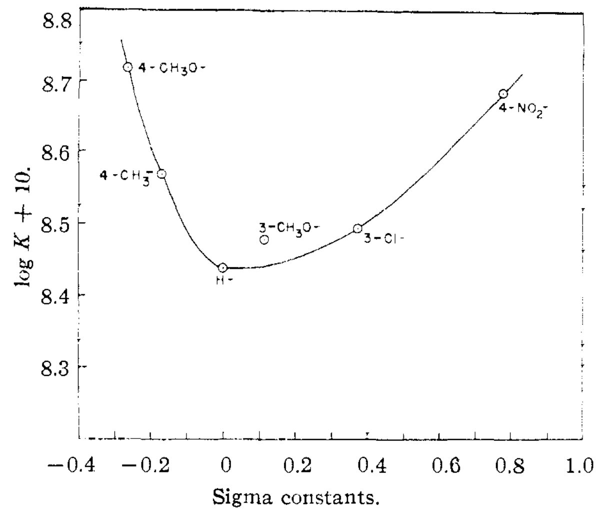


Fig. 2.—Plot of stability constants of substituted platinum–styrene complexes *vs.* sigma values $X\text{-}C_6H_4\text{-}C_2H_3 + (C_{12}H_{24}PtCl_3)^- \rightleftarrows C_{12}H_{24} + (X\text{-}C_6H_4\text{-}C_2H_3PtCl_3)^-$.

Although the steric characteristics of 1-dodecene and styrene are quite different, they probably do not play a decisive role in the relative stabilities of their platinum complexes. The group attached to the ethylenic portion of each molecule extends above the plane of the complex, where no other groups are present with which it might create steric interactions. The difference in stability should lie in the platinum–olefin bond itself.

Since molecular orbital theory has been most useful in theoretical considerations of the metal–olefin bond, it can be employed to compare the platinum complexes of 1-dodecene and styrene. Because the symmetry characteristics of the bonds will be the same in all cases, the variables will be limited to the changes in overlap and energy. In order to form a stable bond the orbitals involved must have an appreciable overlap and nearly equal energies.

If it is assumed that the energies of the pi bonding and antibonding orbitals of dodecene are essentially the same as the known values for ethylene, it can be shown that the overlap integrals for the coördinate sigma bond involving overlap of the pi bonding orbital of dodecene and the 5d6s6p² hybrid orbital of platinum is given by the equation

$$S = \sigma^{\mathrm{Pt-D}} = 1.42 \int \phi_1 \phi_{\mathrm{Pt}} d\tau \qquad (11)$$

where ϕ_1 is the wave function of an ethylenic carbon-atom and ϕ_{Pt} is the wave function of the platinum dsp² orbital and 1.42 is the sum of the coefficients with which the two ethylenic carbon atom *p* orbitals enter the pi molecular orbital of ethylene. The overlap integral for the coördinate or dative pi bond can be shown to be

$$S = \pi^{\mathrm{Pt-D}} = 1.42 \int \phi_1 \phi'_{\mathrm{Pt}}\, d\tau \qquad (12)$$

where ϕ'_{Pt} is the wave function of the platinum 5d6p hybrid orbital.

From the known energy levels for styrene,[11] calculations of the overlap integrals of platinum and this ligand also can be approximated. If $S_\sigma^{\mathrm{Pt-L}}$ and $S_\pi^{\mathrm{Pt-L}}$ represent the overlap integrals for the platinum-styrene sigma and pi bonds, respectively,

TABLE IV

EQUILIBRIUM CONSTANTS STARTING WITH THE 1-DODECENE COMPLEX

$$(C_{12}H_{24}PtCl_3)^- + X\text{-}C_6H_4\text{-}C_2H_3 \rightleftarrows (X\text{-}C_6H_4\text{-}C_2H_3PtCl_3)^- + C_{12}H_{24}$$

Temperature = 25.0 ± 0.2°

X	Concn. of HCl, mole/l.	Anal. wave length, mμ	*K*
H	0.0099	304	0.027 + 0.0004
4-CH$_3$	.0095	314	.037 ± .0008
3-CH$_3$O	.0090	320	.030 ± .001
4-CH$_3$O	.0089	332	.052 ± .0008
4-NO$_2$	.0099	360	.048 ± .002
3-Cl	.0095	306	.031 ± .0006

TABLE V

EQUILIBRIUM CONSTANTS STARTING WITH THE SYTRENE COMPLEX

$$(X\text{-}C_6H_4\text{-}C_2H_3PtCl_3)^- + C_{12}H_{24} \rightleftarrows (C_{12}H_{24}PtCl_3)^- + X\text{-}C_6H_4\text{-}C_2H_3$$

X	Concn. of HCl, mole/l.	Temp., °C.	*K*
H	0.0097	26.0 ± 0.2	0.027 ± 0.0016
4-CH$_3$O	0.0105	25.0 ± 0.2	0.052 ± 0.001

the values are

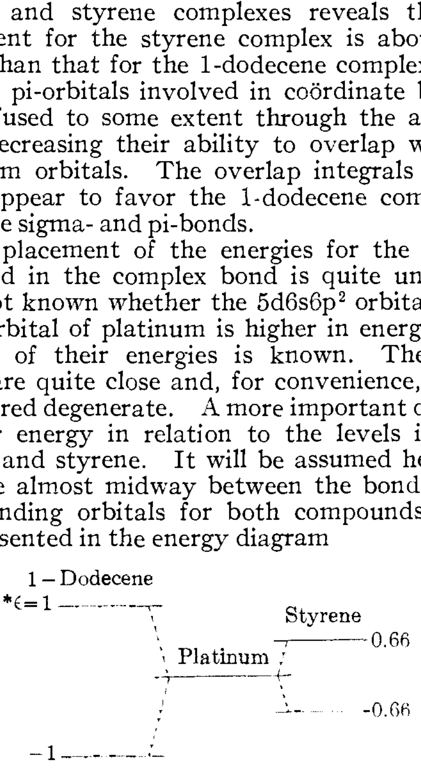
$$S = \sigma^{\mathrm{Pt-L}} = 0.99 \int \phi_2 \phi_{\mathrm{Pt}}\, d\tau \qquad (13)$$

$$S = \pi^{\mathrm{Pt-L}} = 0.99 \int \phi_2 \phi'_{\mathrm{Pt}}\, d\tau \qquad (14)$$

where ϕ_2 is the wave function of either of the exocyclic ethylenic carbon atoms of styrene, and 0.99 is the sum of the coefficients of the contributions of the 2pπ atomic orbitals of the two exocyclic carbon atoms, to the highest occupied (and also the lowest unoccupied) molecular orbital.

Comparison of the overlap integrals for the dodecene and styrene complexes reveals that the coefficient for the styrene complex is about 30% lower than that for the 1-dodecene complex. The styrene pi-orbitals involved in coördinate bonding are diffused to some extent through the aromatic ring, decreasing their ability to overlap with the platinum orbitals. The overlap integrals accordingly appear to favor the 1-dodecene complex in both the sigma- and pi-bonds.

The placement of the energies for the orbitals involved in the complex bond is quite uncertain. It is not known whether the 5d6s6p² orbital or the 5d6p orbital of platinum is higher in energy, since neither of their energies is known. They very likely are quite close and, for convenience, will be considered degenerate. A more important question is their energy in relation to the levels in 1-dodecene and styrene. It will be assumed here that they lie almost midway between the bonding and anti-bonding orbitals for both compounds. This is represented in the energy diagram



*ε = molecular orbital energy.

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[11] H. H. Jaffé, THIS JOURNAL, **77**, 274 (1955).

If this placement is reasonably close to the correct one then the energy should favor the styrene complex in both sigma- and pi-bonds, since the styrene energy levels will both be closer to those of platinum. On this basis it would appear that the overlap loss in the styrene complex, as compared to the 1-dodecene complex, may be cancelled by an appreciable gain in energy. The stabilities of the two complexes should then be expected to be of the same order of magnitude. This is observed in solution, although the equilibrium decidedly favors the 1-dodecene complex. However, the position of equilibrium may be determined to a large extent by the difference in solvation energies for the two complexes.

The influences of substituents on the stability of the platinum–styrene complexes can be considered from two points of view. The first is rather simple, being based on the assumption that the stability of the coördinate sigma-bond is dependent upon the total charge density of the pi-electrons in the exocyclic double bond of the styrene. Thus, high electron density would mean that the ligand was a good donor, able to form a strong sigma-bond. Then, as the Hammett plot is followed in the direction of increasing sigma-constant, the loss in stability from the 4-methoxystyrene complex to the unsubstituted styrene complex could be explained by the decrease of stability in the sigma-bond. The increase in stability observed in moving from the styrene complex to the 4-nitrostyrene complex then would be explained by stabilization of the coördinate pi-bond. The smoothness of the curve and the simplicity of the explanation make this a desirable concept. The principal objection to it is that the total charge density involves the charges in all four occupied orbitals of the styrene, whereas only one orbital can overlap with the $5d6s6p^2$ orbital of the platinum.

The second method of considering the substituted styrene complexes is an extension of the treatment used in the comparison of the 1-dodecene and styrene complexes. Predictions cannot be made easily for the substituted styrenes themselves. However, calculations performed on model styrene compounds, which indicate qualitatively the net inductive and resonance effects of the substituents on the charge densities and energies of the molecular orbitals, led consistently to predictions that the changes in the energy and in the overlap would be opposed. Thus, any stabilizing or destabilizing effect of a substituent on the overlap will be cancelled by an opposite effect upon the energies. Considered from this point of view predictions of substituent effects on stability are difficult to make, but the small size of the effects is not surprising. The opposing effects also offer an explanation of the minimum observed in the Hammett plot.

Experimental

Preparation of Styrenes.—Styrene, 4-methoxystyrene, 4-nitrostyrene and 3-chlorostyrene were purchased from Eastman Kodak, Rochester, New York; Monomer–Polymer Company, Leominster, Massachusetts; and Aldrich Chemical Company, Milwaukee, Wisconsin. With the exception of the 4-nitrostyrene the compounds were distilled under reduced pressure through a four-inch vacuum-jacketed column. 4-Nitrostyrene was recrystallized from a chloroform–heptane mixture, 25% chloroform by volume.

3-Methoxystyrene, 3-nitrostyrene and 4-methylstyrene were prepared according to the method of Brooks.[12]

Preparation of Complexes.—1,3-Bis-(ethylene)-2,4-dichloro-μ-dichloro-diplatinum.—Twenty-five grams of potassium tetrachloroplatinate(II), K_2PtCl_4, was dissolved in 125 ml. of 4% aqueous hydrochloric acid in a bottle which was then mounted on a Parr gas apparatus. The metal gas inlet tube of the apparatus was replaced by a glass tube to prevent contamination from the attack of hydrochloric acid on the metal. The system was flushed with nitrogen and then filled with ethylene to a gage pressure of 45 p.s.i. The bottle was shaken for 36 hr., more ethylene being added as necessary to maintain the pressure near 45 p.s.i. The course of the reaction was followed by the change of the color of the solution from deep red to yellow. When the reaction was complete the solution was filtered and the filtrate was placed in a vacuum desiccator containing sulfuric acid and a dish of potassium hydroxide pellets. Total evaporation of the solvent left a mixture of crystals of Zeises' salt, potassium chloride and a very small amount of unreacted starting material.

The complex then was converted to the dimeric compound by Chatt's method.[4] The crystal mixture was taken up in 4% alcoholic hydrochloric acid to make a solution of Zeise's acid, $H(C_2H_4PtCl_3)$. The undissolved material was removed by filtration. The filtrate was set into a water-bath whose temperature did not exceed 45° and the alcohol was evaporated to dryness under reduced pressure. The complex acid decomposed spontaneously to form the product, $(C_2H_4PtCl_2)_2$. The product was recrystallized from benzene, forming fine orange crystals which decomposed above 160°, without melting.

1,3-Bis-(styrene)-2,4-dichloro-μ-dichlorodiplatinum.—The styrene complex was prepared by a modification of Anderson's method.[2] One millimole of ethylene platinous chloride was mixed with about 20 ml. of hot benzene. Two millimoles of styrene was added and the mixture was heated to boiling, dissolving all of the complex. The solution was filtered hot and permitted to cool, causing rapid crystallization of the product. It was separated by filtration and washed with petroleum ether. It then was recrystallized from benzene and washed again with petroleum ether, yielding fine orange crystals, m.p. 169–171°, with decomposition.

1,3-Bis-(3-methoxystyrene)-2,4-dichloro-μ-dichlorodiplatinum.—One millimole of ethylene platinous chloride was dissolved in about 25 ml. of a warm chloroform–ether mixture. Two millimoles of 3-methoxystyrene was added and the solution was heated to boiling. After cooling to room temperature the product slowly crystallized. It was separated by filtration and recrystallized from toluene. The product was in the form of fine bright orange crystals, m.p. 193–194°, with decomposition.

Anal.[13] Calcd.: C, 27.0; H, 2.52. Found: C, 27.8; H, 2.77.

1,3-Bis-(4-methoxystyrene)-2,4-dichloro-μ-dichlorodiplatinum.—This compound was prepared in the same manner as the 3-methoxystyrene complex. The product was recrystallized from chloroform with the aid of a small quantity of ethyl ether, yielding a bright orange powder, m.p. 192–193°, with decomposition.

Anal. Calcd.: C, 27.0; H, 2.52. Found: C, 26.7; H, 2.47.

1,3-Bis-(3-nitrostyrene)-2,4-dichloro-μ-dichlorodiplatinum.—The 3-nitrostyrene complex could not be purified conveniently by recrystallization because of its limited solubility. To isolate it in acceptable purity the following procedure was used: two millimoles of freshly distilled 3-nitrostyrene was added to about 25 ml. of a warm filtered benzene solution containing one millimole of ethylene platinous chloride. The solution was heated to boiling and then allowed to cool, causing crystallization of the product. Filtration and washing with petroleum ether yielded a pale yellow-orange powder, m.p. 225–225.5°, with decomposition.

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[12] L. A. Brooks, THIS JOURNAL, 66, 1295 (1944).

[13] All ultimate analyses were performed by Geller Laboratories, Bardonia, New York.

Anal. Calcd.: C, 23.1; H, 1.70; N, 3.37. Found: C, 23.7; H, 2.02; N, 3.15.

1,3-Bis-(4-nitrostyrene)-2,4-dichloro-μ-dichlorodiplatinum.—This compound was prepared in the same manner as the 3-nitrostyrene complex. The product was a yellow-orange powder which decomposed above 160°, without melting.

Anal. Calcd.: C, 23.1; H, 1.70; N, 3.37. Found: C, 22.4; H, 1.67; N, 2.81.

1,3-Bis-(3-chlorostyrene)-2,4-dichloro-μ-dichlorodiplatinum.—This complex was prepared in the same manner as the styrene complex. The product was a light orange powder which decomposed above 130°, without melting.

Anal. Calcd.: C, 23.8; H, 1.74. Found: C, 25.1; H, 2.08.

1,3-Bis-(4-methylstyrene)-2,4-dichloro-μ-dichlorodiplatinum.—This compound was prepared, in toluene solution, in the same manner as the 3-nitrostyrene complex. The product was an orange powder which decomposed above 165°, without melting.

Anal. Calcd.: C, 28.2; H, 2.62. Found: C, 28.2; H, 2.94.

1,3-Bis-(1-dodecene)-2,4-dichloro-μ-dichlorodiplatinum.—One millimole of ethylene platinous chloride was dissolved in the minimum volume of warm acetone. Two millimoles of 1-dodecene was added and the solution was warmed until evolution of ethylene stopped. A large volume of petroleum ether was added and the solution was boiled to reduce volume, after which it was cooled to promote crystallization. The product was filtered and recrystallized from petroleum ether, yielding a pink-orange material having a soapy consistency, m.p. 73–74°, with deepening of color but no apparent decomposition.

Anal. Calcd.: C, 33.2; H, 5.57. Found: C, 33.2; H, 5.42.

Ultraviolet Absorption Spectra.—The absorption spectra were obtained with a Beckman DU quartz spectrophotometer. Readings were taken at intervals of 2 mμ or less in the regions of the spectrum showing appreciable absorption. The spectra of some of the dimeric complexes were obtained in both chloroform and *t*-butyl alcohol. The spectra of the ionic complexes were obtained by dissolving the corresponding dimers in an acidic medium, either alcoholic or aqueous hydrochloric acid.

Spectrophotometric Evaluation of Equilibrium Constants.—Before the study of an equilibrium reaction was made, the spectra of the absorbing species involved were rechecked in 0.01 molar anhydrous alcoholic hydrochloric acid over the appropriate portion of the spectrum. A solution of the olefinic reagent in 0.01 molar alcoholic hydrochloric acid was made from freshly distilled material,[14] usually on the day before a run was made. No difficulties were encountered from polymerization of the styrenes. However, these solutions were checked to ensure that the absorbances were constant from the time that they were prepared until they were used.

A solution of the freshly crystallized complex, usually 4.0 × 10^{-3} molar, in 0.01 molar alcoholic hydrochloric acid, was made just before a run was started. Aliquots of 5 ml. of this solution were pipetted into five 50-ml. volumetric flasks. Aliquots of the olefin solution were added to the flasks in progressing volume. Thus, when the flasks were brought to volume, the total complex concentration was 4.0 × 10^{-4} molar in each case, whereas the total olefin concentration varied over a rather wide range. As soon as the volume in each flask had been brought to 50 ml. with 0.01 molar alcoholic hydrochloric acid, a sample was removed and its absorbance was measured in the spectrophotometer, thermostated at 25°. The flask was then suspended in a constant temperature bath at 25° for 1–2 hr. A second set of measurements then was recorded. These usually differed very slightly from the initial readings, indicating that equilibrium had been attained in the few minutes required to prepare the solutions. Absorbance measurements were taken at two or three wave lengths as a check, although it was necessary to use only one value to determine the concentrations of all components in equilibrium.

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(14) 1-Dodecene was used directly as received from Humphrey-Wilkinson, Inc.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED SCIENCE AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Relative Stabilities of Isomeric *cis*- and *trans*-Olefin Complexes with Platinum(II)

BY JOHN R. JOY AND MILTON ORCHIN

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Styrene–platinum(II) complex was equilibrated successively with *cis*- and *trans*-4-methyl-2-pentene and the equilibrium constants measured spectrophotometrically. The data show that the *cis*-isomer is about twice as stable as the *trans*-isomer and slightly more stable than the analogous complex with *cis*-2-pentene.

Introduction

The unequivocal proof of the non-identity of the platinum–olefin complexes from *cis*- and *trans*-isomers of a particular olefin (2-butene) has only recently been reported.[1] We also succeeded some time ago in preparing different complexes from 4-methyl-*cis* and 4-methyl-*trans*-2-pentene and wish to report now our studies on the relative stabilities of these complexes.

In the present work, the equilibrium constants for the reaction of the olefin–platinum complexes with styrene were determined according to the reactions

$$(\mathrm{UnPtCl_2})_2 + 2\mathrm{HCl} \longrightarrow 2\mathrm{H(UnPtCl_3)} \qquad (1)$$

$$\mathrm{PhCH{=}CH_2} + (\mathrm{UnPtCl_3})^- \rightleftharpoons \mathrm{Un} + [\mathrm{PhCH{=}CH_2PtCl_3}]^- \qquad (2)$$

where Un represents the olefin under study. The expression for the equilibrium constant, which was evaluated spectrophotometrically according to the preceding paper,[2] is

$$K = \frac{[\mathrm{Un}][\mathrm{C_6H_5CH{=}CH_2PtCl_3}]}{[\mathrm{PhCH{=}CH_2}][(\mathrm{UnPtCl_3})^-]} \qquad (3)$$

Experimental

1,3-Bis-(*cis*-2-pentene)-2,4-dichloro-μ-dichlorodiplatinum.—Four millimoles of cold *cis*-2-pentene[3] was stirred with one millimole of ethylene platinous chloride, $(\mathrm{C_2H_4PtCl_2})_2$, in about 15 ml. of cold chloroform. The mixture was allowed to come to room temperature, during which all solid material dissolved. The solution then was heated carefully to remove

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(1) H. B. Jonassen and W. B. Kirsch, THIS JOURNAL, **79**, 1279 (1957).

(2) J. R. Joy and M. Orchin, *ibid.*, **81**, 304 (1959).